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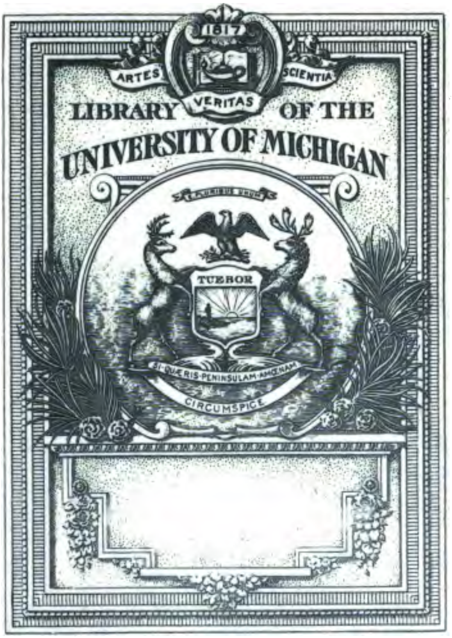

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LABORATORY EXERCISES

WITH

PRIMARY AND STORAGE CELLS

BY

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Assistant Professor of Physics, University of Michigan

GEORGE WAHR
PUBLISHER AND BOOKSELLER
ANN ARBOR, MICHIGAN
1903

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PREFACE

The need of a laboratory manual which I have long felt in teaching the subject of primary and storage cells, has induced me to write this little book. As Carhart's "*Primary Batteries*" is used as a textbook, the subject is treated here only from the practical side. Since the course is primarily intended for students of electrical engineering, advanced exercises belonging more properly to a course in pure electrochemistry have been omitted.

I am greatly indebted to Professors H. S. Carhart and G. W. Patterson, Jr. for aid and advice during the preparation of the book.

KARL E. GUTHE.

ANN ARBOR, MICHIGAN,
February, 1903.

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CHAPTER I.

PRELIMINARY EXERCISES.

Exercise 1. Thermochemical and Electrochemical Processes.

The chemical process of dissolving zinc in dilute sulphuric acid is represented by the equation

$$Zn + H_2SO_4,\ aq. = ZnSO_4,\ aq. + H_2 + 150 \times 10^{10}\ ergs, \qquad (1)$$

where the chemical symbols not only serve to characterize the substance, but denote in addition the internal energy of one gram molecule of the substance. The meaning of formula (1) is therefore: When two gram equivalents, *i. e.* 65.4 grams of zinc, are dissolved in dilute sulphuric acid, zinc sulphate solution containing 161.5 grams of zinc sulphate is formed, 2 grams of gaseous hydrogen are developed and in addition energy equal to 150×10^{10} ergs or 150,000 joules is set free. This energy will usually appear as heat and may be measured in calories. In general, spontaneous chemical reactions take place in such a direction that heat is produced.

In a similar way we may write

$$Zn + CuSO_4, aq. = ZnSO_4, aq. + Cu + 206 \times 10^{10}\ ergs. \qquad (2)$$

The chemical process will take place from the left to the right, but not in the opposite direction, unless we increase the energy of the right hand side, as for example, by the application of a difference of potential sufficiently high to force a current from the copper to the zinc.

In order to show that a process may take place in both directions, the sign $\rightleftharpoons$ is frequently used instead of the equality sign, thus

$$Zn + CuSO_4,\ aq. \rightleftharpoons ZnSO_4, aq. + Cu \pm 206 \times 10^{10}\ ergs. \qquad (3)$$

Frequently a reaction does not continue to completion, in which case $\rightleftharpoons$ should always be used instead of the symbol $=$.

The dissociation theory teaches that, in the two processes considered, zinc goes into solution in the form of ions, *i. e.* each atom, originally without an electrical charge forms an ion carrying a positive electrical charge. If n is its valency, one gram ion carries $n\,q$ coulombs, where $q = 96580$ coulombs. One gram ion of zinc acquires thus in the above processes a positive charge of 193160 coulombs. We say the zinc is oxidized and we shall define oxidation of a body as an increase of its positive electrical charge or a decrease of its negative charge, while reduction of a body consists in an increase of its negative or a decrease of its positive charge.

Since electrical energy is the product of quantity of electricity into a difference of potential, the energy change of one gram atom of zinc passing into the ionic state can be represented by

$$Zn + 2qv_1 = \ddot{Zn}, \qquad (4)$$

where the two dots above the chemical symbol represent the positive charge and v_1 the difference of potential between the metallic zinc and the electrolyte (1 volt × 1 coulomb = 1 joule = 10^7 ergs).

In a similar way we can deduce the equations

$$\begin{aligned} & 2\dot{H} - 2qv_2 = H_2\,, \\ \text{and} \quad & \ddot{Cu} - 2qv_3 = Cu\,. \end{aligned} \qquad (5)$$

The hydrogen in process (1), as the copper in (2), undergo therefore a reduction, since they lose their positive charge in passing from the ionic into the metallic state.

There may be other changes besides those of an electrical nature, and we cannot in general assume the latter to be alone present. Writing ± A ergs for the energy changes not due to electrical action, we can write equations (1) and (2) in the usual electrochemical notation :

$$Zn \left\| \begin{matrix} \dot{H} \\ \dot{H} \end{matrix} \; \bar{S}\bar{O}_4 \rightleftharpoons \ddot{Zn} \; \bar{S}\bar{O}_4 \right\| H_2 + 2q(v_2 - v_1) \pm A_1\, ergs, \qquad (1^a)$$

and

$$Zn \,\|\, \ddot{Cu} \; \bar{S}\bar{O}_4 \rightleftharpoons \ddot{Zn} \; \bar{S}\bar{O}_4 \,\|\, Cu + 2q(v_3 - v_1) \pm A_2\, ergs. \qquad (2^a)$$

The fact that the electrolyte never acquires a free electrical charge, shows that oxidation cannot take place without a corresponding reduction going on at the same time. If the oxidation of zinc and the reduction of hydrogen or copper, occur at the same point, for example, when we immerse a zinc rod in sulphuric acid or copper sulphate solution, no free electrical charge can be developed, since that given up by the reduced body is acquired by the oxidized zinc, and the energy change $2q\,(v_2-v_1)$ will appear as heat. We have then a thermochemical reaction.

But if we devise some means for separating the places at which oxidation and reduction occur, as in a voltaic cell, then positive charges will disappear at the zinc electrode and appear at the other electrode and an electromotive force, E. M. F., is produced, equal to v_2-v_1 volts, and an electric current will pass, if an external metallic circuit is completed.

To illustrate the foregoing considerations, perform the following experiments:

(a) Fill a glass beaker half full of copper sulphate solution. Invert in it a test tube filled with the same solution and containing a few strips of zinc. Observe the reaction taking place. Repeat with quite dilute solution, test the gas developed and write out the chemical equations.

Does a reaction like this take place in a Daniell cell? If so, can it contribute to the electrical current furnished by the cell?

(b) Fill a large test tube half full with copper sulphate solution, insert a thermometer reading to 1/5 ° C. and add some zinc dust. Stir with the thermometer and observe the rise in temperature.

(c) Put a porous cup into a glass jar. Fill both with acid-free* zinc sulphate solution. Immerse inside the porous cup an amalgamated zinc rod, and outside a platinum strip, covered with platinum black, and join the two through a voltmeter (see below).

Add one or two cubic centimeters of sulphuric acid to the side *with the platinum electrode.* Measure the E. M. F. of the cell and explain why we have a voltaic reaction, though the acid does not act directly on the zinc.

Repeat the exercise, but add the acid to the solution in the porous cup. Explain why there is no increased E. M. F.

This experiment is known as Ostwald's experiment to show chemical action at a distance.

After completing the exercise pour the solution into the bottle, marked "Zn SO_4 after use." This bottle contains zinc strips which will remove most of the sulphuric acid from the solution.

---

* If the $Zn\ SO_4$ solution does not contain free acid there will be only a slight E. M. F. which will rapidly decrease to less than 0.1 volt when the electrodes are for a short time short circuited. Should there be an appreciable amount of free acid it may be removed by the following method: The solution is electrolysed between platinum electrodes (or a platinum cathode and zinc anode) with a small current density. On standing, the zinc deposited at the cathode will act upon the acid readily. Carhart, *Electrical World*, 26, p. 551, 1895.

The electrodes while not in use should be kept in an acid-free Zn SO_4 solution. Oxidation of the electrodes is certain to introduce a difference of potential. Gases dissolved in the electrolyte are also troublesome.

A copper plate may be used instead of platinum, but the effect of the acid will not be as marked owing to the rapid polarization of the copper surface.

VOLTMETERS AND AMMETERS.

Voltmeters and ammeters are usually portable galvanometers of the d'Arsonval type and are direct-reading instruments, that is, they are so calibrated as to show directly upon an arbitrary scale the difference of potential existing, or the current flowing between any two points to which they may be connected.

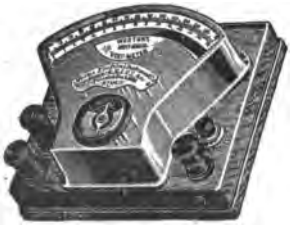

Fig. 1.

The best known instruments of this class are those designed by Weston. In these the directing force is furnished by two spiral springs of phosphor-bronze. Rapid damping is secured by the use of aluminum frames upon which the coils are wound. The voltmeter (Fig. 1) is commonly provided with two scales, one for high and one for low voltages. In the figure the low voltage terminal on the negative (left hand) side is marked 15. The binding post on the right hand side belongs to both scales and is always to be connected to the positive electrode. The push button seen just above this binding post makes contact when pressed down and can be kept in this position by a slight turn of the knob.

The Weston instruments are durable and remarkably accurate. The student should thoroughly familiarize himself with them before attempting to use them independently.

FORM OF RECORD.

Exercise 1. To study the difference between thermochemical and electrochemical processes.

Room -------- Date ------------------

(a) Displacement of copper by zinc.

(1) Concentrated solution. --------------------------

(2) Dilute solution ------------------------------

(b) Heat effect of chemical reaction.

(c) Voltaic effect of chemical reaction.

Exercise 2. Influence of Concentration upon the Electromotive Force.

A porous cup is placed inside a larger glass jar and both are filled two-thirds full with a solution of Zn SO_4. Be careful to have no free acid. Two well amalgamated zinc rods serve as electrodes, one inside the porous cup, the other in the outer solution. This cell is connected in series with a key, a galvanometer and a resistance of at least 2000 ohms. The latter is introduced, to make the change of the internal resistance of the cell, produced by the dilution of the electrolyte, as small as possible as compared with the total resistance of the circuit. For the same reason a siphon connecting two separate jars should not be used.

Since the E. M. F. obtained might produce a deflection too large to be read, it is best to adjust the galvanometer beforehand by means of a shunt, in such a way that for concentrated solution in the porous cup and hydrant water outside, the reading will still be on the scale.

With solutions of the same concentration on both sides, there should be no deflection of the galvanometer, or only a small one. Dilute the solution in the glass jar to 1/2, 1/4, etc. to 1/64 of the original concentration and observe the deflections. Each time the zinc electrodes should be rubbed clean, since they oxidize easily.

Find the direction of the current by substituting a Leclanche element for the concentration cell, and since the former has a very large E. M. F. compared with the latter, the galvanometer must be shunted by a small resistance (1 ohm), before the Leclanche cell is put into the circuit.

Compare results with Nernst's theory and apply them to a Daniell cell.

FORM OF RECORD.

Exercise 2. To study the influence of concentration upon the electromotive force.

Room-------- Date-------------------

Galvanometer-------- Shunt--------

Concentration.		Deflections and their direction.
In porous cup	In glass jar	

Test with a Leclanche cell:

Conclusions:

Exercise 3. Influence of Temperature upon the Electromotive Force.

Fill two beakers with $ZnSO_4$ solution and connect the two by a siphon, (Fig. 2). The amalgamated zinc rods used as electrodes are connected with a fairly sensitive galvanometer and a resistance in circuit if necessary. Measure the temperature of the solu-

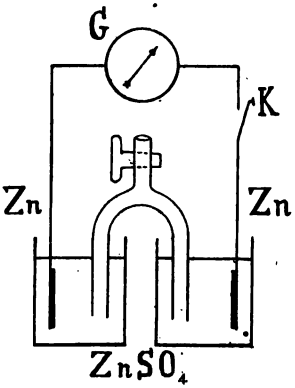

Fig. 2.

tions by means of ordinary thermometers.

With temperatures equal on both sides there should be no deflection. Cool or heat the electrolyte in one beaker, observe the deflections of the galvanometer and read the thermometers. Take 8 to 10 steps, closing the key *K* not longer than necessary for observation. Before every reading clean the zinc electrodes.

In order to adjust the sensitiveness of the galvanometer, a preliminary adjustment of the resistances, similar to that in the preceding exercise, should be made with hot and cold solutions.

To find the direction of the current, substitute a Leclanche element, but note the precaution mentioned in Exercise 2.

Plot the differences in temperature and the deflections. Compare the results with Nernst's theory and apply them to the Daniell cell.

FORM OF RECORD.

Exercise 3. To study the influence of concentration upon the electromotive force.

Room-------- Date-------------------

Galvanometer--------

Temperature		Deflections and their direction
Beaker 1	Beaker 2	

Test with a Leclanche element:

Conclusions:

Exercise 4. Electromotive Force with Pure and Impure Mercury.

Since the slightest trace of metals like zinc which are far removed from mercury in the voltaic series, changes the electrical behavior of mercury, the object of this exercise is to study the influence of zinc upon the potential difference between mercury and an electrolyte.

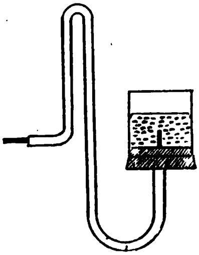

Fig. 3.

Pure mercury is poured into cups formed by a short glass tube closed at the bottom by a cork through which the end of a rubber covered copper wire passes, as shown in Fig. 3. These cups are lowered into the electrolyte, dilute sulphuric acid saturated with mercurous sulphate, Hg_2SO_4. The latter is only slightly soluble, (0.05%).

The two electrodes are joined through a voltmeter or a galvanometer of small sensitiveness. There should be no deflection if pure mercury is in both cups.

Now add to the mercury in one cup a *very small* piece of zinc scraped from an amalgamated rod or plate, observe the deflection, add a little more zinc, and so on, until the deflection is nearly constant. If the experiment is intended to give quantitative results, prepare a zinc amalgam of definite concentration and add from this to the known amount of mercury in one cup.

Since mercury polarizes very rapidly when the circuit is closed, it is best to put a little solid Hg_2SO_4 as a depolarizer on top of the pure mercury. The mercury in either cup may also be stirred by a thin glass rod.

Substitute for the impure mercury an amalgamated zinc rod and observe the deflection. It should be borne in mind, that while a slight trace of the zinc produces a large E. M. F. between the pure and impure mercury, the amalgam will act as a zinc electrode only when it is saturated, *i. e.*, when some zinc is in the solid form. This point is reached when the zinc forms about 1.5% of the amalgam.

To purify mercury, it usually suffices to shake it in a separatory funnel with a 5% solution of mercurous nitrate, a little nitric acid being added. After the first shaking open the glass stopper. Then shake from 10 to 30 minutes longer, according to the conditions. The mercury must then be washed with distilled water, best in a second separatory funnel (not hydrant water which would produce a layer of calomel) and finally it is filtered through thick filter paper with a pin hole at the bottom in order to remove the last traces of water. Thus metals replacing mercury from its solutions are removed; silver or gold can be removed only by distillation in a partial vacuum.*

The following method has been found convenient for cleaning small quantities of impure mercury and illustrates at the same time an interesting topic in the study of cells, namely, local action. Pour on the washed mercury a fairly concentrated solution of sulphuric acid and stir the mercury with a carbon rod or let it stand for some time with the rod in the mercury. A voltaic cell is formed consisting of zinc, acid and carbon, with the electrodes short circuited. Explain the process by which the mercury is purified.

FORM OF RECORD.

Exercise 4. To study the influence of zinc upon the electrical behavior of mercury.

Room........ Date....................

Voltmeter No........

No. of pieces of Zn added	Voltage

Voltage with Zn rod as negative electrode....................

Exercise 5. The Terminal Potential Difference as a Function of the External Resistance.

The terminal potential difference of a cell depends upon its electromotive force and upon the drop of potential inside the cell. The E. M. F. equals the sum of all the single potential differences arising at the junction of different electrical conductors, the most important being those between the electrodes and electrolytes, while those between different electrolytes are in general very small.

---

* Ostwald-Luther, *Physiko-chemische Messungen*, 2nd ed. p. 130, or Hulett, *Ztschr. Phys. Chemie* 33, p. 620, 1900.

The electromotive force, E, depends upon the current only so far as polarization may be produced by the latter. The influence of polarization is treated in Exercise 9, but will be neglected until then.

The drop of potential over a certain part of an electrical circuit is the product of its resistance into the current.

The terminal potential difference, E', of a battery equals the E. M. F., minus or plus the drop of potential inside the cell, according as the current is produced by the cell itself or is sent through it from some other source in a direction opposed to its own E. M. F.

If r denotes the internal resistance of the battery and I the current

$$E' = E \mp Ir\,. \tag{6}$$

The terminal potential difference equals therefore the E. M. F. of the cell, if it is on open circuit, and, if a current is produced by the cell itself, the internal resistance must decrease with increase of current, *i.e.*

decrease of external resistance, until it finally becomes zero when the cell is short circuited and $I = \frac{E}{r}$.

Consider the case of a Daniell cell which is represented in Fig. 4, where the potentials are given as ordinates and the resistances as abscissae.

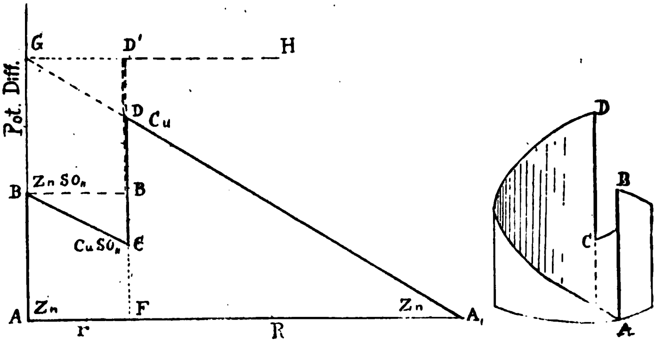

Fig. 4.

The potential of the zinc being the lowest in the whole circuit, is represented by the point *A*. Between the Zn plate and the $ZnSO_4$ solution there is a sudden rise in potential of 0.52 volt, so that the potential of the $ZnSO_4$ solution next to the Zn plate is represented by the point *B*. Then follows a drop in potential in the cell until the Cu electrode is reached when a second sudden rise of 0.58 volt occurs, the potential of the $CuSO_4$ next to the copper plate and that of the Cu electrode being represented by the points *C* and *D* respectively. From the copper plate, the potential falls off regularly owing to the external resistance R until the zinc plate is again reached at A_1.

To complete the analogy, the figure should be considered as wound upon the surface of a cylinder so as to make A_1 coincide with A. If both solutions are normal there is no appreciable difference of potential between the liquids themselves. The electromotive force, E, of a cell is the sum of the potential differences at the plates, *i. e.*, $AB + CD =$ AG, while the value of the terminal potential difference E', is represented by FD, and depends upon the E. M. F. and the relative values of the external and internal resistances, R and r.

Since
$$E = I\,(R + r) \tag{7}$$
if all electrical energy is spent in the form of heat
$$E' = E\,\frac{R}{R + r}. \tag{8}$$

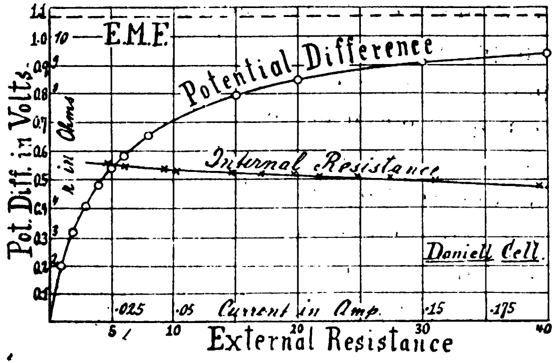

Fig. 5.

Plotting E' as ordinates and R as abscissae the terminals, and is observed by a microscope having instead of the crosswires a micrometric scale of 30 divisions. For distinctness it is best to have the capillary as near the wall of the larger vessel as possible. Good illumination is also required.

Since the mercury runs out of the capillary easily it is of advantage to bend the capillary up so as to form a U tube and adjust the mercury so that it stands a few millimeters from the outer end. (Hulett).

The mercury in the capillary moves easily only if the tube is well wetted with the sulphuric acid. For this reason draw the mercury up a little before beginning the measurements. This may be done by careful suction or by adjusting the pressure on a closed rubber tube which is attached to the end of the glass tube. A little acid on top of the mercury column is also of advantage.

The instrument is well fitted for zero methods, but can be used to measure differences of potential, not higher than 0.01 volt, since within this limit the changes in the position of the meniscus may be considered proportional to the change in the difference of potential without introducing a large error (see Exercise 8).

The direction of the applied difference of potential should always be such that the small electrode forms the cathode, *i. e.*, becomes charged possitively, since otherwise the mercury gets dirty and its motion becomes sluggish. If this has happened, press a little mercury out of the capillary by increasing the pressure.

Anodic polarization will decrease the surface tension of the mercury and the meniscus will therefore move towards the electrolyte.

If not in use, the instrument must be kept short circuited, (key *K*, Fig. 10).

Exercise 8. Temperature--Coefficient of a Cell.

The E. M. F. of a cell varies with the temperature and it is therefore customary to refer it to the value which it has at a definite temperature, for example, 15° C., (or 20° C., as with cadmium standard cell). The formula for the E. M. F. may be written

$$E_t = E_{15} \pm \alpha\,(t-15) \pm \beta\,(t-15)^2 \qquad (15)$$

Usually only the first correction term comes into account, and α is the total change of E. M. F. in volts per degree Centigrade.

The older form

$$E_t = E_{15}\,[1 \pm \alpha'\,(t-15)\,] \qquad (16)$$

is still in frequent use where $\alpha' = \frac{\alpha}{E_{15}}$. Both expressions of α have been called the temperature coefficient.

In general the E. M. F. changes only slightly with the temperature. For its measurement a sensitive method, like the potentiometer method (Exercise 7), must be employed, but it may be simplified somewhat by using the capillary electrometer (p.24). In the electrometer described, a change of one scale part in the position of the mercury meniscus corresponds to a change in difference of potential of 0.0001 to 0.0005 volt, according to the size of the capillary, and small changes in the E. M. F. — up to 0.01 volt — may be considered proportional to to the change in the position of the meniscus.

Determine the temperature coefficient of a sal ammoniac cell, consisting of a zinc and a carbon electrode in a small glass vessel containing a NH_4Cl solution, the whole standing in a larger waterbath. Begin at a temperature of 15° C. Measure the E. M. F. of the cell, *E*, by the potentiometer method, using the electrometer instead of the galvanometer. After having obtained a balance a small change in the resistances of the boxes *R* and *R'* (Fig. 9), sufficient to produce a change of about 0.005 volt in the potential difference, will produce a corresponding change in the position of the meniscus.

From this calculate the difference of potential corresponding to a movement of the mercury through one division of the micrometer scale.

Now restore the balance for 15° C. and heat the cell by steps to 30° C., reading for each temperature the position of the meniscus. From these readings calculate the change in E. M. F. of the cell, $\triangle E$, and the temperature coefficients a and a'.

Plot E. M. F. and temperatures.

FORM OF RECORD.

Exercise 8. To determine the temperature coefficient of a sal ammoniac cell.

Room--------   Date-------------------

Resistance boxes No---------

Balance with standard cell:

Calibration of capillary electrometer:

R.	E.M.F.	Change in R.	Change in E.M.F.	No. of scale div.	Value of one sc div.

Experimental cell:

Temp.	R.	E.	Sc. div.	$\triangle E$	a	a'
------	---------	---------	---------	---------	------	------
------	---------	---------	---------	---------	------	------
------	---------	---------	---------	---------	------	------

Exercise 9. Polarization of a Cell.

The E. M. F. of a cell is subject to changes due to the current flowing through the cell. These changes, the causes of which are manifold, are called "polarization" and since they tend to decrease the current we speak of the "counter E. M. F." of polarization, which must always be subtracted from the original E. M. F. in order to give the effective E. M. F. In all calculations of electrical quantities in a circuit containing a cell this effective E. M. F., and not the original E. M. F. should be used.

Deposition on the electrodes of a substance different from that of the plates is one of the main factors of polarization. This is very apparent in the simple voltaic cell, consisting of a zinc and a copper plate in dilute sulphuric acid. When the circuit is closed, zinc goes into solution, hydrogen ions collect at the copper plate and even penetrate into the plate, (occlusion).

The exercise consists of two parts, namely the study, first, of the influence of the size of the copper electrode upon the rapidity of polarization and, secondly, of the influence of occlusion in the copper plate of the hydrogen ions.

Prepare two copper plates of different size, say 4 cm^2 and 9 cm^2. Cover the back, and especially the place to which the lead wire is soldered, by shellac. The plate should be entirely immersed in the liquid. The size of the zinc electrode is of little account for the following.

(1) Connect the simple voltaic cell having the small copper plate as positive electrode directly to a voltmeter, close the circuit at a definite time and read the voltmeter, at first every 10 seconds, later at longer intervals. Continue polarization for twenty minutes.

(2) Repeat after having cleaned the zinc,

with the larger copper plate as electrode.

(3) At the end of 20 minutes clean the zinc, take the copper plate out of the solution and rub off the hydrogen under water, replace the electrode and take a new series of observations for twenty minutes. It will be seen that now the polarization is much more rapid, due to the occlusion of the hydrogen in the electrode.

Frequently the first part of the curve is not as steep as later, especially if copper plates are used that have been for some time in contact with air, showing the presence on the electrodes of a substance acting as a depolarizer. To prevent this, Cu should be deposited by electrolysis on the plate, the latter after being taken out of the solution, quickly washed in water, immersed in alcohol and dried in air.

Plot the three curves obtained, the voltmeter readings as ordinates and the time as abscissae.

FORM OF RECORD.

Exercise 9. To study the polarization of a simple voltaic cell.

Room-------- Size of Plates { ----- ------- / ------------- } Date------------

Small Plate		Large Plate, 1st Test		Large Plate, 2nd Test	
Time	Reading in Volts	Time	Reading in Volts	Time	Reading in Volts

CHAPTER III.

MEASUREMENT OF INTERNAL RESISTANCE.

Exercise 10. Measurement of the Internal Resistance of Cells. (Modification of Mance's Method.)

If in the Wheatstone bridge arrangement

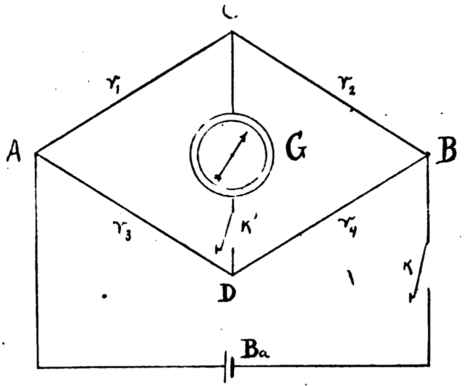

Fig. 11.

(Fig. 11), the relation

$$r_1 : r_2 :: r_3 : r_4 \qquad (17)$$

is satisfied, a change in E. M. F. or in the resistance of one of the remaining two branches *AB* and *CD* will have no influence upon the difference of potential and the current in the other. The two branches are therefore called conjugate and contain in the usual arrangement, one the cell and the other the galvanometer. In this case, if relation

(17) is satisfied, no current will flow through the galvanometer, and thus a method is afforded for measuring the resistance of one of the four arms r_1, r_2, r_3, r_4.

By placing the cell in one of the arms, say r_1, and substituting for it in *AB* a short circuiting key, we have a method for measuring the resistance of a cell, because relation (17) must hold, if on closing this key, *i. e.*, changing the resistance of *AB* from infinity to zero, the current through the galvanometer does not change. Under this condition

$$r = r_1 = r_2 \frac{r_3}{r_4}. \tag{18}$$

There are however, grave objections to the method in this form, the principal objection being that as a relatively large current is taken from the cell itself, a possible variation of the galvanometer deflection due to the polarization of the battery may result.

A simple modification avoids this difficulty. The arrangement of the apparatus is shown in Fig. 12. Instead of sending a steady current through the ballistic galvanometer *G*, it is connected in series with a condenser of large capacity, *C*. After short circuiting the galvanometer by a key shown in the figure, the key K_1 is closed and the condenser charged to a difference of potential pro-

(Fig. 5), we obtain, if E and r are constant, a rectangular hyperbola, whose asymptotes are $x = -r$ and $y = E$.

To measure a potential difference E between two points, they are connected to the terminals of a condenser of capacity C, which is then charged with a quantity of electricity $Q = EC$. If now this connection is broken and the condenser connected with a ballistic galvanometer G, we obtain in the latter a deflection proportional to the quantity of electricity discharged through it, or, if C remains constant, proportional to the potential difference E.

$$d = \frac{1}{c} Q = \frac{1}{c} EC = kE . \tag{9}$$

k may be found by charging and discharging the condenser with a known E. M. F.*

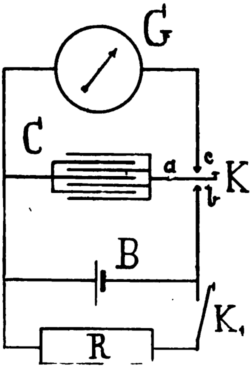

Fig. 6.

The arrangement of the apparatus is shown in Fig. 6, and a convenient form of

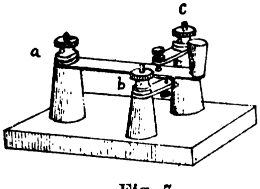

Fig. 7.

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[*] For the theory of the ballistic galvanometer the student is referred to Carhart and Patterson, *Electrical Measurements*, p. 207.

charge and discharge key, denoted by K_2, is shown in Fig. 7.

Find the terminal potential difference of a Daniell cell as a function of external resistance, which is varied by the following steps: 60, 40, 20, 10, 6, 4, 2, 1, 0.5, 0.3, 0.1 ohms. If necessary the resistance of the lead wires must be taken into account. Assume for the determination of the constant K, that the E. M. F. of the Daniell cell is 1.1 volts.

Plot the results as shown above (Fig. 5), also r as a function of I, calculating these quantities from the equations

$$r = \frac{E-E'}{E'} R, \tag{10}$$

and

$$I = \frac{E'}{R}. \tag{11}$$

r may be found directly from the curve for the potential difference, because $r = R$, if $E' = \frac{E}{2}$.

To set up a Daniell cell, first fill the porous cup containing the amalgamated zinc, or negative electrode, two-thirds full of zinc sulphate solution and wait until the solution begins to moisten the outside of the cup before placing the cup in the glass jar containing the copper, or positive electrode, and the copper sulphate solution. In order to avoid changes in the internal resistance during the experiment it is well to short circuit the cell for ten minutes before using.

After use the cell must be taken apart, the zinc sulphate poured back into its bottle, the porous cup thoroughly washed and *the zinc rubbed clean.* Copper oxide is usually deposited on the zinc as a black film. This may be readily rubbed off while it is moist, but if it be allowed to dry, it adheres firmly and renders it difficult to amalgamate the zinc again. The E. M. F. of a Daniell cell is about 1.1 volts and this value may be used in all cases where great accuracy is not required.

If the test is made with a cell easily polarized, *e. g.*, a dry cell, it is better to use instead of the charge and discharge key a pendulum apparatus which mechanically closes the circuit, charges and discharges the condenser and opens the circuit again in a definite, very short time. The pendulum apparatus is described in Exercise 14.

FORM OF RECORD.

Exercise 5. To determine the terminal potential difference of a Daniell cell as a function of the external resistance.

Room........

Date....................

Galvanometer......................

Condenser ....

Resistance Box....................

Deflection with open cell...........

Constant of galvanometer..........

R	d	E′	I	r

CHAPTER II.

MEASUREMENT OF ELECTROMOTIVE FORCE.

Exercise 6. Measurement of E. M. F. of a Cell. First Method.

The voltmeter reading indicates the difference of potential between the terminals. If we connect the electrodes of a cell to the voltmeter, the latter will give the E. M. F. of the cell only if the external resistance, *i. e.*, the resistance of the voltmeter, is very large compared with the resistance of the cell (see Exercise 5).

Weston voltmeters, reading to 3 volts, have a resistance of 250 to 300 ohms and with cells having an internal resistance of 3 ohms, an error of 1% would be made, if the reading of the voltmeter should be taken as the E. M. F. of the cell. For cells with still higher internal resistance the error will be proportionately higher.

In the following method using an auxiliary cell this error is avoided, since no current flows through the cell, whose E. M. F. is to be measured.

The apparatus (Fig. 8), consists of a cell, *B*, of E. M. F. higher than that of the cell to be measured, a resistance *R*, and a voltmeter *V*. The cell *B'*, whose E. M. F. is to be determined, is joined in parallel with the voltmeter, so that its E. M. F.

has the same direction as that of the cell *B*. Close key K_2, and adjust the resistance *R*, until on closing K_2, the reading of the voltmeter does not change. In this case no current is going through battery *B′* and the reading of the voltmeter gives us directly the E. M. F. of the cell *B′*.

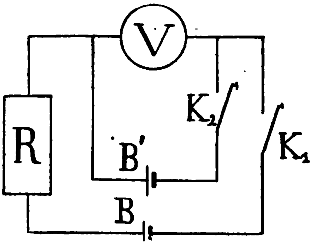


Fig. 8.

Measure the E. M. F. of 5 cells, including old dry cells. Use both methods, the usual, *i. e.* with key K_1 open and only K_2 closed, as well as that given in this exercise. Compare the results.

FORM OF RECORD.

Exercise 6. To measure the electromotive force of five different cells by means of a voltmeter.

Voltmeter-------- Date------------------

	E. M. F. found	
Name of cell	without auxiliary cell	with auxiliary cell

Exercise 7. Measurement of the E. M. F. of Cells by the Potentiometer Method.

In measurements of E. M. F. or of potential difference where a high degree of accuracy is required, it is necessary to compare the E. M. F. to be measured with that of a standard cell.

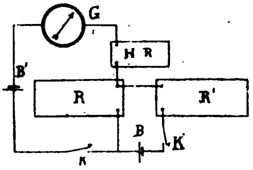


Fig. 9.

The arrangement of the apparatus is shown in Fig. 9. The principle of the method consists in producing by means of a current from the battery B, a potential difference at the terminals of a resistance R, equal to the E. M. F. of the cell B' whose electromotive force is to be measured. The two electromotive forces should be so arranged as to oppose each other in the galvanometer branch. If now the keys K and k be closed, no current will flow through the galvanometer and $E = i\,R$. In practice a standard cell is first placed at B'. Let its known E. M. F. be E_1; then $E_1 = i_1 R_1$. The cell under experiment is next set in at B', and after the resistance has been so adjusted that no current flows through the galvanometer on closing the keys, we have

$$E_2 = i_2 R_2, \tag{12}$$

and under the condition that $i_1 = i_2$, we have at once

$$E_2 = E_1 \frac{R_2}{R_1}. \tag{13}$$

The condition $i_1 = i_2$ is fulfilled when the battery B has a constant E. M. F., *and when the sum of the resistances R and R' remains constant throughout the experiment.* It is moreover apparent that the E. M. F. of B must be greater than that of B'. A pair of Daniell cells or a storage cell is best for this purpose. If the E. M. F. of ordinary open circuit cells is to be measured, a freshly charged Leclanche element will do very well, as the high resistance of $R+R'$ prevents it from polarizing appreciably, if the key K is kept closed for but an instant. The high resistance *H. R.*, is inserted in the galvanometer circuit to prevent the passage of large currents through the instrument. It should be cut out when a balance is nearly obtained. R and R' are high resistances, *e. g.*, 10,000 ohms, and their sum is kept equal to the maximum resistance in one box.

It is clear that a wire of constant length and uniform cross-section may be substituted for the two resistances R and R', and a balance obtained by shifting one terminal of the galvanometer along the wire. If the readings are a_1 and a_2 in the two cases, then

$$E_2 = E_1 \frac{a_2}{a_1}. \tag{14}$$

In this case however, care must be taken to avoid heating the wire, and to this end the key K should be kept closed but an instant at a time.

FORM OF RECORD.

Exercise 51. To measure the E. M. F. of five cells by the potentiometer method.

Date--------------------

	Name of cell.	R	R′	E
Galvanometer --------	-------------	------	------	------
Room-----------------	-------------	------	------	------
Resistance boxes------	-------------	------	------	------
Standard cell No------	-------------	------	------	------
Temperature ---------	-------------	------	------	------

THE CAPILLARY ELECTROMETER.

In the above exercise the galvanometer was inserted in the circuit to indicate the presence or absence of a current. The balance being obtained there is no difference of potential between the terminals of the galvanometer.

The capillary electrometer may be used for this purpose instead of the galvanometer. Its construction is based upon the change of the surface tension of mercury in contact with an electrolyte, if the potential difference at its terminals is changed. It consists of two mercury electrodes, of which one is large and at the bottom of a small glass vessel, about three-quarters full of dilute H_2SO_4, (1:6), saturated with Hg_2SO_4, while the other electrode is in a glass tube whose lower end has been drawn out into a fine capillary (Fig. 10). The tube is filled with mercury so that the lower meniscus stands a few millimeters from the end of the capillary, the height of the mercury in the tube depending upon the size of the capillary. The best height, 20 cms., can easily be obtained by adjusting the length of the capillary.

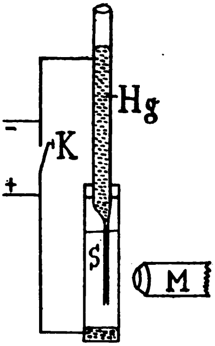


Fig. 10.

A movement of the meniscus in the capillary will follow a change of the potential difference at duced by the current through r_3 and r_4. Now open the short circuit key and close K_2. Then close the short circuit key again and open K_1 and K_2. Adjust the resistances until on closing K_2 there is no deflection of the galvanometer. Then

$$r = r_2 \frac{r_3}{r_4}. \qquad (19)$$

The closing and opening of the keys should be done in rapid succession. Resistances r_3 and r_4 should be rather large in order to make the current small.

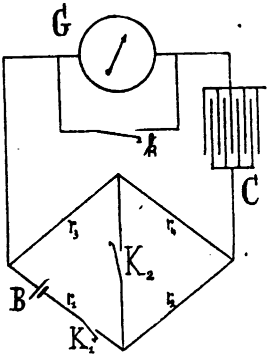


Fig. 12.

Measure the resistances of five different cells by this method.

FORM OF RECORD.

Exercise 10. To measure the resistance of five different cells by Mance's method.

Room--------

Date--------------

Galvanometer--------------------

Condenser ----------------------

Name of Cell	r_2	r_3	r_4	r

Exercise 11. Measurement of Internal Resistance of Cells by Nernst and Haagn's Method.

In this method the internal resistance of the cell is determined by means of an alternating current, while the cell itself furnishes no current whatever. In this way the disturbing effects of polarization are entirely avoided. The alternating current is furnished by the induction coil *I* (Fig. 13), which charges the condenser *C* alternately to positive and negative potentials. These alternations are transmitted to a Wheatstone bridge, of which the condensers C_1 and C_2 form two arms, and a slide-wire bridge in series with the cell, the other two.

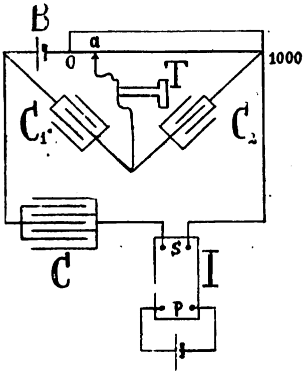


Fig. 13.

Since an alternating current passes through the bridge we have to substitute a telephone for the galvanometer of the ordinary bridge arrangement. As long as a current passes through the telephone a sound is heard in it.

Connect one terminal of the telephone to the contact maker of the bridge and move the latter along the bridge wire until there is no sound in the telephone.

Let r' be the sum of the resistances of the battery (r) and the portion of the bridge wire from the battery to the contact maker, and R' the resistance of the rest of the bridge wire.

The applied variable difference of potential due to the induction-coil produces at any given moment a current i through the resistances R' and r'. Condenser C_1 will be charged with a quantity $C_1 i r'$, and condenser C_2 with a quantity $C_2 i R'$. For a minimum sound in the telephone these charges are equal or

$$C_1 i r' = C_2 i R', \tag{20}$$

or

$$r' = \frac{C_2}{C_1} R'. \tag{21}$$

The resistance of the bridge wire must be known. If it is R ohms, then the resistance of one division on the bridge $s = \frac{R}{1000}$; and if the contact maker is a scale divisions from the end of the wire next to the battery

$$\text{and} \qquad \begin{aligned} r' &= a \,.\, s + r \\ R' &= (1000-a)s \,. \end{aligned} \tag{22}$$

The expression for the internal resistance of the battery becomes then

$$r = \left\{ \frac{C_2}{C_1} (1000 - a) - a \right\} s . \qquad (23)$$

Kohlrausch's bridge as used for the measurement of the resistance of electrolytes* is well suited for this experiment. For most accurate results it is best to make a as small as possible. Sometimes, especially if very small battery resistances are measured, it is of advantage to shunt the bridge wire by a small resistance, S, say one ohm, thus reducing the value of one unit of the bridge to $s = \frac{1}{1000} \frac{R\,S}{R + S}$.

If the exact ratio of the condensers is unknown, it may be found by connecting them directly to the ends of the bridge and balance as before. Let the bridge reading in this case be b scale divisions.

Then

$$\frac{C_2}{C_1} = \frac{b}{1000 - b} , \qquad (24)$$

and

$$r = s \, \frac{b - a}{1000 - a} . \qquad (25)$$

This method is admirably suited for the measurement of the resistance of storage cells.

Measure the resistance of five different cells by this method.

---

* Reed and Guthe, *Manual of Physical Measurements*, p. 139.

FORM OF RECORD.

Exercise 11. To measure the internal resistance of five different cells by Nernst and Haagn's method.

R.......... s.......... Date..........

Name of Cell	C_1	C_2	a	R′	r	r

Exercise 12. Measurement of the Internal Resistance of Cells by the Voltmeter and Ammeter Method.

If no polarization takes place, the electromotive force E, terminal potential difference E', external resistance R, and internal resistance r, are connected by the equation

$$r = \frac{E - E'}{E'} R , \tag{26}$$

or since the current I equals E'/R, we may also write

$$r = \frac{E - E'}{I} . \tag{27}$$

The internal resistance of a battery can therefore be found by a measurement of E, and of E' while the circuit is closed through a known resistance R, or while a known current I is flowing through it.

Both methods may be used at the same time and afford a good check one to the other.

The simplest way to measure E and E' is by means of a voltmeter, and I by means of a milliammeter, but we have seen that a voltmeter should be used only with cells of low internal resistance. Besides as some time is required to read the instruments, polarization may set in, thus making the results for this very convenient method more or less unreliable, especially for a cell, which polarizes rapidly.

We shall apply the method to a Daniell cell only, and study the change of its internal resistance due to changes in temperature. The Daniell cell used in this exercise consists of a copper cup as electrode, containing the $CuSO_4$ solution and the porous cup with the zinc electrode and the $ZnSO_4$ solution. The porous cup should be clean. (To set up a Daniell cell, see p. 18.)

The cup may be heated directly over a flame. Before a measurement is made the solutions inside and outside the porous cup must be at practically the same temperature. The apparatus is set up as shown in Fig. 14, where *V* is the voltmeter, *A* a milliammeter and *R* a resistance box. Take the readings *E* of the voltmeter with key *K* open, and *E′* and *I* of the voltmeter and the ammeter with the key closed. Select the resistance *R* so that *E′* is about one-half of *E*.

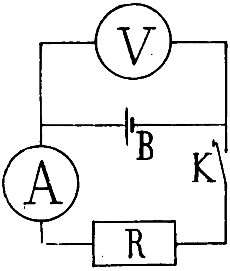


Fig. 14.

Vary the temperature of the cell by steps from 5°C. to 30°C., stirring the $CuSO_4$ solution and the crystals with a glass rod, so as to facilitate saturation.

Calculate the internal resistance by both formulae (26) and (27), adding to R the resistance of the wires and the milliammeter, which may for all practical purposes be assumed to be 0.2 ohm.

The E. M. F. of a Daniell cell does not change appreciably with the temperature, while the internal resistance depends on two factors, first, the increase of conductivity of the electrolyte with an increase of temperature and, second, the increase of concentration of the solution.

To bring this out more clearly, repeat the exercise with $CuSO_4$ solution, saturated at about 5°C., but not containing an excess of crystals.

How does this apply to the Clark and the Carhart-Clark standard cells?

Plot the internal resistance as a function of the temperature in the two cases.

FORM OF RECORD.

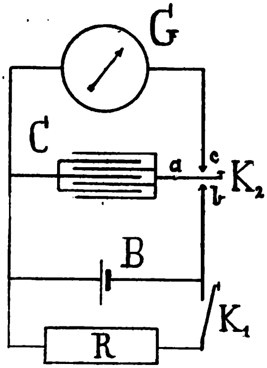
Exercise 13. To measure the internal resistance of a Daniell cell as a function of the temperature by the voltmeter and ammeter method.

Voltmeter........ Ammeter........ Date..............

Saturated Solution.					Unsaturated Solution.				
temp.	E.	E′.	R.	r.	temp.	E.	E′.	R.	r.

Exercise 13. Measurement of the Internal Resistance of Cells by the Condenser Method.*

The principle of this method has been employed in Exercise 5 and the apparatus is to be arranged in the same way as there (Fig. 15). With K_1 open, charge and discharge the condenser C through the ballistic galvanometer G, then close K_1 and immediately afterwards charge and discharge the condenser. Let the two deflections obtained be d_1 and d_2. From the considerations of Exercise 5 follows that



$$r = R\,\frac{d_1 - d_2}{d_2} \qquad (28)$$

For the determination of the internal resistance it is best to choose the external resistance such as to make d_2 about one-half of d_1.† If the resistance of the cell is smaller than one ohm, it is better to make R at least one ohm, since otherwise the polarization will be too rapid and introduce a large error.

Take for each cell three different resistances and make three observations with each resistance.

---

* Carhart, *Primary Batteries*, p. 115.

† Carhart and Patterson, *Electrical Measurements*, p. 101.

If it is required to obtain E in volts the condenser is charged from a standard cell also and discharged through the galvanometer. Let the deflection in this case be d', and let d_1 be the deflection given by the cell under investigation when on open circuit. The deflections are proportional to the quantities of electricity passing through the galvanometer, and these are themselves equal to the product of the difference of potential at the terminals of the condenser times the constant capacity C. Therefore if E_s be the E. M. F. of the standard cell, then

$$E = E_s \frac{d'}{d_1} . \qquad (29)$$

The following modification of the preceding method has been proposed.

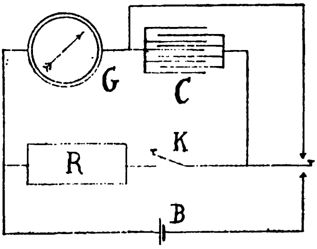


Fig. 16.

The apparatus is arranged as in Fig. 16. In this case the condenser is charged through the galvanometer, the resulting deflection being proportional to the potential difference charging the condenser. To obtain E the key K should be open; to determine E', it should be closed. It is claimed that this modification gives better results since the reading is taken at the instant the circuit is closed and polarization only very small. Both methods agree however very closely in their results.

Measure the internal resistance of three different cells by both methods.

FORM OF RECORD.

Exercise 13: To measure the internal resistance of three cells by the condenser method.

Room...... Date..............

Galvanometer....................

Name of cell	First method				Second method			
	d_1	R.	d_2	r.	d_1	R.	d	r.

Exercise 14. Variation of the Internal Resistance of a Cell with the Current.

The internal resistance of cells as measured by the condenser method is not a constant, but decreases, especially in the case of dry cells, with increase of the current. In order to obtain quantitative comparisons for such cells, it is necessary to devise some mechanical means to control the time during which the circuit is closed. Carhart's "pendulum apparatus" is admirably suited for the purpose and is described in the following way:*

---

* Carhart and Patterson, *Electrical Measurements*, p. 179.

"A rectangular frame carries at the bottom a heavy pendulum bob adjustable in height. The time of vibration of this is about one second. The bob is held in place by a detent. When it is released it swings between two parallel circular arcs, concentric with the axis of suspension. The distance apart of these arcs is a little less than the length of the lower cross bar carrying the heavy bob. They support four keys, which can be clamped at any desired points. The keys have an upper and lower contact like a simple discharge key. When the key lever is erect the key makes contact on the lower point; and when the lever is thrown over by the cross bar of the pendulum as it swings forward, the key makes contact on the upper point. These keys can be set in any relation to one another which may be desired and their operation is controlled entirely by the pendulum. Thus the time during which the cell is kept closed through the resistance may be made very short, and the condenser may be charged and discharged during this short interval of time. By this means polarization is reduced to a minimum and uniformity is secured.

The connections for making a measurement of internal resistance is shown in Fig. 17. The pendulum is supposed to swing from left to right. When it strikes the lever or detent of key *1* contact is made on the upper point and this closes the battery circuit through a known resistance *R*. The overturning of the lever of key *II* puts the two terminals of the battery in connection with the condenser *C*. When the pendulum reaches *III* and overturns its detent lever, the battery is removed from the condenser and contact with the upper point causes a discharge through the galvanometer *G*. Finally on passing *IV* the pendulum operates this key and opens the battery circuit."

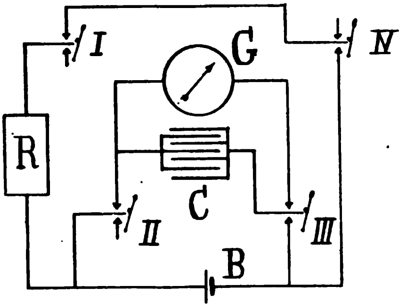


Fig. 17.

In this manner we obtain a deflection, d_2, proportional to the terminal potential difference. To obtain d_1, proportional to *E*, it is necessary to open keys *I* and *IV*, and use only *II* and *III*.

After each reading the pendulum is brought back to the detent at the left and the levers are then set up *in the order in which they are thrown over by the pendulum.* Why?

For a connection which will always keep the circuit closed, instead of open as shown here, see Exercise 15, Fig. 18.

In this exercise we use only the connections as shown in Fig. 17. Determine d_1 and d_2 for a cell, whose resistance has been measured by Nernst and Haagn's method, varying the external resistance from 60 to 1 ohm. Calculate r from equation (28) and plot r as a function of $I = E'/R$. Repeat the experiment, changing the position of key I so as to vary the time during which the circuit is closed.

The result shows a variation of the internal resistance with the current, but this is probably due to polarization, whose influence is neglected in formula (28).

Taking polarization into account it is found that the real resistance of the cell is very nearly the lowest resistance obtained by the condenser method, *i. e.*, the one corresponding to the largest currents.* This value agrees well with that found by Nernst and Haagn's method.

The condenser method may therefore be used for finding the counter electromotive force due to polarization of a cell whose internal resistance is known.

Denoting by e the counter E. M. F. of polarization and by b the real resistance of the cell, the complete formula would read

---

* Guthe, *Physical Review*, VII, p. 103, 1898.

$$b = \frac{E - e - E'}{E'} R = r - \frac{e}{I}, \tag{29}$$

and $$e = (r - b) I. \tag{30}$$

Calculate e from the above formula, using for b the value found in Exercise 11, and plot the polarization in the two cases as a function of the current I.

FORM OF RECORD.

Exercise 14: To determine the apparent variation of the resistance of a cell with the current, and the counter E. M. F. of polarization.

Room-------- Date--------------
Galvanometer-------- Defl. with standard cell------------
Condenser-------- Cell-------- b= ------ (exercise 11.)

	d_1	R	d_2	E′	r	I	r–b	e

CHAPTER IV.

TIME TESTS.

Exercise 15. Time Test of a Cell.*

The time test of a cell is intended to give us: (1) its rate of polarization when closed through a definite external resistance, (2) the promptness and extent of recovery from polarization, (3) the internal resistance and its rate of change.

In order to obtain these quantities we have to measure the E. M. F. and the terminal potential difference, not alone for "zero" time, *i. e.*, with the cell on open circuit, but also while the current is flowing, *i. e.*, when the circuit is closed through a known external resistance. In order to obtain the E. M. F. in this case, the circuit must be opened just long enough to take an observation and then immediately closed again.

After polarization has continued sufficiently long, 40 minutes or 1 hour, the circuit is broken and the recovery of the cell obtained by observing the E. M. F. alone for a definite time interval.

Since during the first part of the polarization, as well as of the recovery, the changes in E. M. F.

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* For a detailed description of the method and examples see Carhart, *Primary Batteries*, pp. 115—131.

are much more rapid than after a few minutes, the first observations should be made at short intervals, 30 seconds or less. Later more time may be allowed between readings.

Methods for obtaining E, E' and r have been described in Exercises 12, 13 and 14. The condenser method is most suitable for it, especially when the pendulum apparatus, described under Exercise 14, is used in connection with it.

For the observations at zero time the four keys of the pendulum apparatus are connected as shown in Fig. 17. We obtain then with keys *II* and *III* alone the E. M. F., and with all four keys the terminal potential difference.

For the time test proper, the connections of keys *I* and *IV* have to be changed so that the circuit is closed when the levers of keys *I* and *IV* are up as well as when they are down. Such a connection is shown in Fig. 18. Keys *II* and *III* are connected the same way as in Fig. 17. With all four levers up, the swinging of the pendulum first opens the circuit (*I*) then charges (*II*) and discharges (*III*) the condenser through the galvanometer and im-

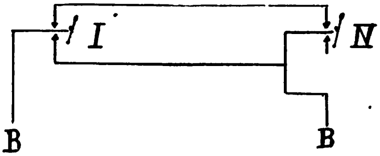

Fig. 18.

mediately afterwards closes the circuit again (*IV*). In this case with all four keys we obtain the E. M. F., with *II* and *III* alone the terminal potential difference.

In order to express these quantities in volts the constant of the galvanometer (see p. 17) must be determined. *

Take a 40 minute polarization and recovery test of a Leclanche cell by means of the condenser method, the external resistance being 5 ohms.

Plot the curves for E, E', r and I as functions of the time; that for the recovery of E being plotted backward on the same sheet of cross-section paper.

FORM OF RECORD.

Exercise 15: To make a polarization and recovery test of a Leclanche cell.

Room-------- Date--------------
Galvanometer------------- Condenser--------
Deflection with standard cell--------------

Polarization							Recovery		
time	d_1	d_2	E	E′	I	r	time	d	E

Exercise 16. Life Test of an Open Circuit Cell.

An open circuit cell is intended to give a current only for a short time and to recover during a longer interval of rest. Intermittent current tests in which the cell is alternately producing a current and on open circuit for a definite period, have been employed, but such tests give hardly more information about a cell than the following method which has the advantage of greater simplicity and of giving a result in a shorter time.

---

* For a convenient graphical method of calculating E and E′ in volts from the galvanometer deflection obtained by a standard cell see Carhart, *Primary Batteries*, p. 120.

The principle is the same as that employed in the last exercise; the cell is kept closed through an external resistance of 10 ohms, and its E. M. F. and terminal potential difference are observed at definite intervals, while r is calculated (equation 26). After the E. M. F. has dropped to less than half its original value, the cell is allowed to recover for a period at least as long as that of polarization. Frequently it is of interest to study in addition the polarization after recovery. This polarization is always very rapid.

The amount of the total electrical energy produced by the current is also of prime importance. Since electrical energy equals the product of difference of potential times quantity of electricity, and the latter equals the current times the time,

$$El.\ Energy = E\,Q = E\,I\,t\,. \qquad (31)$$

The E. M. F. and current I vary during the test, and the average value must be used, which may be found by dividing the time into intervals in which the variation is linear, and take half the sum of the values at the beginning and at the end of this interval as the average. If we select in the expression for the electrical energy the hour as the unit of time, we obtain the result in watt-hours. Plot the curve for the watt-hours produced by the cell. Similarly a curve for the available energy, equal to $E'It$ may be calculated and plotted. It is apparent that this quantity depends on the relative values of external and internal resistances.

The results obtained from tests of this kind combined with the original cost of the cell allow a very good estimate of their comparative value, no matter for what purpose they are to be used.

The amount of zinc used or the waste of material is only of secondary importance with such a cell, since it becomes practically useless after having run down.

Make a life test of a dry cell using the voltmeter method for finding r (Exercise 12).

FORM OF RECORD.

Exercise 16: To make a life test of a dry cell.

Voltmeter______________ Date____________

External Resistance____________________

Polarization							Recovery	
Time	E	E′	r	I	It	Energy	time	E

Exercise 17. Efficiency Test of Closed Circuit Cell.

In the last exercise we have seen that a given cell can furnish only a definite amount of electricity.

Dry cells are practically useless after they have once been exhausted, but other cells may be used again after the materials in the cell have been renewed.

For the complete test of such a cell we have to take a polarization test as described in Exercise 16 and in addition calculate the efficiency in ampere-hours as well as the cost per watt-hour furnished by the cell.

To deposit one gram equivalent of zinc, *i. e.*, one half of 65.4 grams, 96,580 coulombs = 26.83 ampere-hours are required. 1.215 grams of zinc correspond therefore to one ampere-hour.

By weighing the zinc before and after the test, we can easily calculate from the loss of zinc the corresponding theoretical number of ampere-hours. From the observations during the life test we obtain the actual output in ampere-hours.

Now the ampere-hour efficiency is

$$Amp.\ Eff. = \frac{actual\ ampere\text{-}hours}{theoretical\ ampere\text{-}hours}.$$

Efficiency may also be expressed as the ratio of the weight of zinc which would be deposited by the quantity of electricity furnished by the cell to the total loss of zinc during the experiment. The difference between the two is the loss by local action, from which the percentage loss can easily be determined.

For all electrical tests of this kind it is however just as important to know the relation of the amount of energy, *i. e.*, watt-hours, to the cost of one charge of the cell. It is quite possible that one cell has a larger percentage loss than another owing to local action, but nevertheless it may furnish a larger amount of electrical energy for the same price.

The watt-hours are calculated in the same manner as in the last exercise.

Set up a bichromatic cell by dissolving 20 grams of $Na_2Cr_2O_7$ in 100 cm^3 of water, adding 20 cm^3 of concentrated H_2SO_4 and using as electrodes a carbon plate and an amalgamated zinc rod. Make a life test of this cell, as described in Exercise 16, with 2 ohms external resistance and calculate in addition the percentage loss of zinc due to local action, the efficiency in ampere-hours and the cost per ampere-hour furnished by the cell. A recovery test is not made with a closed circuit cell.

FORM OF RECORD.

Exercise 17: To make an efficiency test of a bichromate cell.

Voltmeter.............. Date................

External resistance.................

Description of cell------------------------

Price of material---------------------

Weight of zinc before-----------------------------

Weight of zinc after-----------------------------

Loss of zinc-----------------

Ampere-hours corresponding to the loss of zinc----------------

Test:

Time.	E	E′	r	I	It	Watthours.

Efficiency = ------

Percentage loss of zinc = ------

Cost of material per watt-hour = ------

Exercise 18. Test of a Storage Cell.

The *efficiency* of a storage cell is the ratio of the amount of available electrical energy given out by the cell when discharging, to the energy necessary to recharge it. Thus

$$\textit{Efficiency} = \frac{\textit{watt-hours given out}}{\textit{watt-hours put in}} = \frac{(E_1 - I_1 r_1)Q_1}{(E_2 + I_2 r_2)Q_2} = \frac{E'_1 Q_1}{E'_2 Q_2}$$

The potential difference is measured by a voltmeter and the current by an ammeter.

Frequently the efficiency is given as the ratio of ampere-hours, *i. e.*, as the ratio Q_1/Q_2, which will of course have a higher value than the above expression, since E'_2 is always larger than E'_1. Efficiency of a storage cell should however be expressed in watt-hours (energy efficiency), not in ampere-hours (quantity efficiency).

The *capacity* of a cell can also be expressed in two ways. It is the number of watt-hours or ampere-hours which the cell is able to give on discharge, *i. e.*, either $E'_1 Q_1$ or Q_1. In practice it is important to know the ratio of the capacity to the total weight of the cell, *i. e.*, the capacity per kilogram or per pound.

Another interesting item is the variation of *internal resistance*, which may be found from the equation

$$r = \frac{E - E'}{I} . \qquad (32)$$

The electromotive force E is determined by opening the circuit just long enough for observation and then closing it again.

Charge a storage cell with the normal* charging current, until its difference of potential has risen to 2.4 volts and then discharge it through a rheostat with the normal discharge current, until the E. M. F. has dropped to 1.8 volts. Observe at intervals E, E' and I, calculate r, the average potential difference E'_1 and Q_1.

Then charge again to 2.4 volts, reading voltmeter and ammeter as before and calculating r, E'_2 and Q_2. Calculate the efficiency in watt-hours, (for comparison also in ampere-hours). Plot the corresponding curves.

---

* The normal charging current is a current which charges the cell in 10 hours.

Repeat the exercise with currents smaller than the normal, and calculate the efficiency in this case.

The above method can be applied without modification to a storage battery consisting of a number of cells.

While tests of this kind are valuable for the study of cells intended for laboratory use, they give us little information as to their fitness for practical work. Storage cells are used for so many different purposes and under such widely varying conditions, that it is impossible to devise a test for all such cells. They must be studied under conditions like those under which they are intended to be used and the tests must be extended over a long period. Such tests are in their nature unsuited for ordinary laboratory exercises.

FORM OF RECORD.

Exercise 18: To test a storage cell.

Voltmeter.......... Date..........
Ammeter..........
Name of cell.............. Weight of cell..........

Discharge					Charge				
E	E′	I	r	Q	E	E′	I	r	Q

Efficiency in watt-hours.......... Efficiency in ampere-hours..........
Total capacity...... Capacity per kilogram weight......

* * *

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